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OBSERVATION OF FeO IN ABSORPTION BY FLASH HEATING AND KINETIC SPECTROSCOPY

by

Arnold M. Bass

Technical Report
to
National Aeronautics and Space Administration
Washington, D. C.

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Preface

The work described in this report was done by the author in collaboration with Dr. L. Nelson and Mr. N. Keubler. The initial experiments -- in the ultraviolet region of the spectrum -- were performed at the Bell Telephone Laboratories, Murray Hill, New Jersey; the experiments in the visible region of the spectrum were performed at the National Bureau of Standards, Washington, D. C. A manuscript based upon this report will be submitted for publication in the Journal of Chemical Physics under the joint authorship of A. M. Bass, N. A. Keubler, and L. S. Nelson.

OBSERVATION OF FeO IN ABSORPTION BY FLASH HEATING AND KINETIC SPECTROSCOPY

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The emission spectrum of the diatomic oxide, FeO, has been studied for a number of years.[1] In extending these studies, several new ways to produce the spectrum in absorption have been examined recently. We report here on the use of flash heating and kinetic spectroscopy[2] for the excitation of the orange system A and B bands of FeO in absorption, and a diffuse absorption feature in the 2410-2430 A region during the direct reaction of metallic iron with gaseous oxygen.

The orange A and B band spectrum of the FeO molecule has been recorded in emission from flames by Howell and Rochester[3] and Garger,[4] from exploding wires by Rosen,[5] and during the flash

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photolysis-induced explosion of iron pentacarbonyl-oxygen mixtures by Erhard.[6] In flash photolysis experiments with ferrocene-oxygen and iron pentacarbonyl-oxygen explosions, Callear and Norrish[7] have observed the orange bands both in emission and absorption, several strong FeO bands in emission in the 8000-10,000 A region, several unidentified features, and a new, rather diffuse feature in emission and absorption lying between 2410 and 2430 A that has been attributed on chemical grounds to FeO.

Delsemme and Rosen[8] and Malet and Rosen[9] have made assignments of the energy levels involved in the discrete banded spectra of FeO.

The flash heating technique uses an intense light pulse from a capacitor discharge lamp to induce rapid high temperature reactions at the surface of a solid of high specific area.[10] Photographic absorption spectra of thermally produced species are recorded through the heated volume by flash spectroscopy[11] after an appropriate delay. The absorption spectrum of PbO recorded this way has been reported previously.[12]

EXPERIMENTAL

Metallic iron was suspended in the optical path either as one meter of 13μ diameter wire wound on a rectangular frame of thin quartz rod,[2] or as 10 strips of 3 mm by 2 cm by 13μ foil held in a step-type quartz holder.[13] Cylinder oxygen was passed slowly through the quartz cell at pressures between 50 Torr and atmospheric.

An Edgerton, Germeshausen, and Grier Corporation "Sun Flash"

capacitor bank, capable of delivering 10,400 joules at 4 kv, was discharged through a helical heating lamp similar to the General Electric Company FT-625. The thermal output has been described earlier.[14]

The following wavelength regions were studied: (1) 1800 to 3000 A, in order to observe the diffuse feature near 2400 A; (2) 4400 to 5200 A, in order to observe, if possible, the weak blue C system; and (3) 5200 to 6000 A, in order to detect the orange A and B system. A 2-meter evacuable spectrograph with a 600 line/mm grating (plate factor 7.51 A/mm) was used for region (1)[2]; a Baird Associates Eagle-mount 2-meter spectrograph with a 1440 line/mm grating (plate factor 3.1 A/mm) was used for regions (2) and (3). Both gratings were used in the first order. A Lyman-type background source, fired at 3.75 μf and 10 kv, was used for region (1); a small sealed-off quartz lamp, operated at 3.75 μf and 8.5 kv, was used for regions (2) and (3). Both lamps were controlled with a thyratron circuit.[15] Eastman Kodak 35mm SWR film or Ilford Q-2 plates were used for region (1); Eastman Kodak 35mm Tri-X film was used for regions (2) and (3).

RESULTS

The most intense absorption of FeO was recorded about 4 to 5 msec after the start of the heating flash (duration about 3 msec). The absorption of atomic iron was most intense at 2 to 3 msec, with hardly any FeO detectable then. Very little discrete absorption was

observed before 2 msec or after 6 msec. It should be noted that these appearance times for FeO in the combustion of solid iron in oxygen are about 10 times greater than those observed in the homogeneous explosions of ferrocene-oxygen[7] and iron pentacarbonyl-oxygen[6,7] mixtures.

In region (3), the A(0,0)i, A(0,0)ii and B(0,0) bands of the orange system at 5614.0, 5582.8, and 5789.8 A, respectively, were clearly detected in absorption, as well as a great deal of fine structure throughout this region. Only a few iron absorption lines appeared here since relatively few lines that arise from low-lying atomic states fall in region (3).

In region (2), more iron absorption lines appeared, but the blue C system could not be detected in absorption, even though the lower state is said to be common with the A and B systems.

A great many iron absorption lines appeared in region (1); also the broad diffuse absorption feature at approximately 2420 A. However, the absorption feature showed no step-wise structure of the type seen in Callear and Norrish's Figure 16.

A continuous darkening of the film appeared in every exposure in regions (2) and (3) where iron and oxygen were present in the cell simultaneously. Instrumental scattered light was eliminated as a possible source of the continuum. In a separate study, high-speed motion pictures (15,000 fps)[16] of iron grids flashed in air at atmospheric pressure showed first a brilliant thermal emission from liquid metal droplets that lasts for about 4 msec after the

start of the heating flash, and a brilliant diffuse background emission that began about 7 msec after the start of the heating flash. In nitrogen, the thermal emission from the droplets was seen for about the same length of time, but the background emission was absent. Thus, the undesirable film darkening seems to arise from an incandescence from both liquid metal droplets and very fine hot oxide particles. This incandescent emission was not observed at the short wavelength end of the spectrum (region 1).

After each experiment, a heavy deposit of orange-red powder was found on the holders and on the cell walls near the reaction zone. Also, in those experiments in which iron foil was used, solidified black droplets of 0.5 to 1.0 mm diameter were found adhering strongly to the holders and cell walls. Presumably, the orange-red powder is Fe_2O_3, while the black material is a mixture of iron and FeO, not unlike that formed on iron meteorites.

The conslusions that can be drawn from these experiments are as follows: (1) the flash heating technique can be used to produce absorption spectra of metal oxides relatively simply by the direct reaction of the metal with gaseous oxygen; (2) the lower state of the A and B bands of FeO is confirmed as the ground state, since it has been observed in absorption in both the homogeneous ferrocene and carbonyl explosions and the heterogeneous iron-oxygen reaction; (3) even though the ultraviolet spectrum we observed differs greatly in appearance from that observed by Callear and Norrish,

the feature at 2410-2430 A seems to occur also in the direct reaction of iron and oxygen, and apparently involves the ground state; and (4) an incandescent cloud of hot iron oxide particles is formed a few milliseconds after the spectrum of the FeO molecule is observed.

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